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RAW MATERIALS

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ENRICHABILITY OF QUARTZ FROM THE ZHURAVLINYI LOG KAOLIN DEPOSIT

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The composition of mineral inclusions in quartz sand of wastes from kaolin production at "Plast-Rifei," operating at the Zhuravlinyi Log deposit, is studied. Different technological operations for enriching this raw material are tested. It is shown that the use of different technological operations for enriching wastes and using them to develop high-purity quartz concentrates suitable for the fabrication of glass is an effective procedure.

Key words: quartz wastes from kaolin production, enrichment, quartz concentrates.

The problem of efficient and comprehensive use of mined raw materials from the Zhuravlinyi Log deposit is of paramount importance for "Plast-Rifei" JSC, just like for many mining enterprises. At the present time this enterprise produces the following: metakaolin — raw material for the production of zeolites and molecular screens, fireclay — raw material for the production of refractory materials, sanitary-technical articles, and decorative objects. The high-silica base is used for the synthesis of catalysts, zeolites, and adsorbents. A premix is required and produced — kaolin-containing product consisting of two main components, kaolinite (47%[5]) and quartz (45%), as well as 8 – 10% alkali-containing and mixed-layered minerals.

Given the yearly production and processing of up to 100,000 tons of raw material and the production of 30,000 tons of goods, the remaining raw material produced, consisting mainly of quartz, is inevitably stored in dumps. It is certainly of great interest to study the possibilities of using such quartz in different areas of industry: construction industry, for the production of technical ceramics, for fabricating different types of glass including quartz glass, in metallurgical production, for synthesis of silicon and different types of silicon compounds.

Russia has enormous deposits of vein quartz and high-silica raw material in the form of quartzites. Deposits of quartz of the highest quality are concentrated in the Urals [1]. It would appear that in this situation there is no great urgency in researching the possibility of using unconventional high-silica raw materials.

But one must keep in mind the fact that quartz deposits are often located in places which are difficult to access. The development of these deposits and the production of raw materials require substantial material resources to develop all forms of the infrastructure of the mining enterprise: roads, energy supply, material-technical base, labor resources, social-housing facilities, and so on. The production of raw materials inevitably leads to environmental degradation as least in the production region. Existing technologies for production and processing of quartz raw materials, the geological-mineralogical particulars of the deposits and the raw material itself, and the production culture lead to 75 – 90% raw materials losses during the creation of high-enrichment quartz concentrates [2].

The arguments given above have initiated an investigation of the possibility of creating highly pure quartz concentrates from the quartz in the wastes at the "Plast-Rifei" enterprise.

A preliminary visual analysis under an optical microscope of washed quartz sands has shown that they consist predominately of grains of transparent, smoky, ferruginous, and dull quartz 0.5 – 4 mm in size. Irregularly shaped grains with oval, smoothed contours are present in small quantities in sharp-angled fragments. Sand and individual quartz pieces

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[5] Here and below — content by weight.

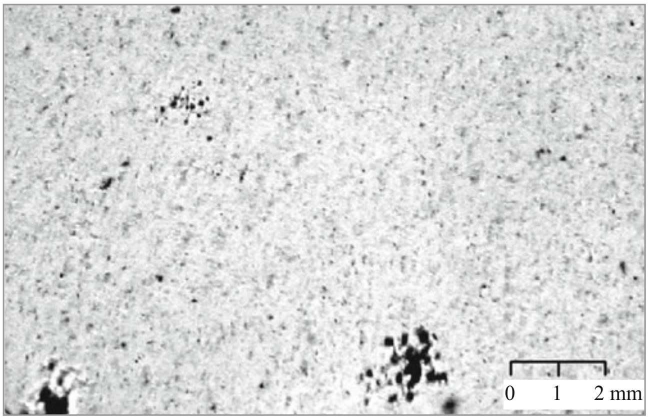

Fig. 1. Shadow photograph of a sample of quartz glass (in the bulk), obtained from the raw materials in the technogenic wastes at "Plast-Rifei" JSC.

contain metallic minerals: ilmenite, rutile, magnetite, and hematite. Most quartz grains possess kaolinite dabs on the surface. Sands contain many different micaceous minerals and appreciable quantities of isometric grains of albite and microcline, agglomerated and pellet-shaped kaolinite, tourmaline, rutile, and sphene. Individual grains of apatite, disthene, and technogenic inclusions are observed. Some grains of quartz have pockets of leached, apparently, feldspar minerals.

The certification criteria for the purity of quartz grains, created by various methods of enriching quartz from technological dumps were structure perfection and optical transparency of quartz-glass blocks made from the grains. Even though such certification does not give unequivocal information about the amount and composition of the mineral and structural impurities in raw material, it does permit evaluating efficiently, accurately, and understandably the technological quality of the raw material and the methods used to enrich it.

The materials were comminuted manually in a quartz mortar and classified into size fractions (< 0.1 > 0.0), (< 0.2 > 0.1), (0.4 > 0.2) mm using laboratory metal sieves. The quartz grains (< 0.2 > 0.1) and (< 0.4 > 0.2) mm were triply magnetic separated by an ÉVS-10/5 electromagnetic separator with magnetization currents of the coils 3, 5, and 10 A. After magnetic separation, to remove the dust-like fraction the grains were flushed with drinking water and dried. The magnetically screened materials were also washed, dried, and analyzed with a binocular microscope. The following materials are present in the material screened by electromagnetic separation for weak magnetic fields: magnetite, hematite, ilmenite, tourmaline, and grains of quartz with limonite. The screenings obtained with strong magnetic fields consist of sphene, rutile, muscovite, and grains of quartz with films of iron hydroxides.

Quartz glass was made from washed and magnetically separated grains by means of vacuum melting [3]. The mass of the block was about 100 g. The glass contained a large number of bubbles ranging in size from fractions to 1 – 2 mm. A substantial quantity of colored and transparent striae and precipitates, similar to those created artificially in the interior volume of high-purity glass, were observed in the glass [4]. A second glass block was made under identical conditions from the preceding raw materials but additionally purified by leaching impurity minerals over 1 h in a 20% solution of hydrofluoric acid at 90 – 100°C. Just as in the preceding experiment, the glass contained bubbles. There were somewhat fewer bubbles but they were larger, and the glass contained virtually no colored striae, except separate spherical precipitates which were blue-gray in reflected light. Judging from the external appearance, the melt formed from the material of these spherules liquated in a melt of quartz glass. The melting temperature of the material was probably higher than the melting temperature of cristobalite. In this case the material of an inclusion solidifies while still inside the quartz glass melt. When the glass solidifies the spherules in its vicinity produce elastic stresses. A qualitative analysis of the chemical composition of the spherules using a JXA-733 microanalyzer with an INCA Energy 200 EDS-spectrometer showed that the inclusions consist of rutile, and containing in individual cases negligible amounts of zirconium, niobium, aluminum, and iron.

One glass was made from grains enriched by agglomeration removal of mineral inclusions [5] followed by etching in 20% solution of hydrofluoric acid at 90 – 100°C. The glass contained bubbles but they were much smaller (by a factor of 2 – 3) than in the preceding cases. It was more pure and there were virtually no inclusions.

Different methods were used to enrich the raw materials and develop a high-purity quartz concentrate. The metric fraction of the grains varied from (< 0.4 > 0.2) to (< 0.2 > 0.1) and (< 0.1 > 0.63) and the composition of the acidic leaching solutions were varied; solutions with hydrofluoric and orthophosphoric acids were used. As a simplification and to reduce the cost of enrichment technology and to decrease the harmful factors of production new operations were introduced and conventional operations were eliminated. Specifically, flotation and separation in heavy liquids were not used; these operations are most complicated, most harmful, and most expensive. To create conditions, which are as close as possible to being identical, for making the certified glasses from grains enriched by various methods, a method of making four to five glasses simultaneously in a single furnace charge, was developed. The glass blocks made were 25 – 25 mm in diameter and 30 – 40 mm high. Glass samples, 10 mm thick, were cut from these blocks perpendicular to the axis and prepared by grinding and polishing for the purpose of investigating their structure and optical characteristics.

Figure 1 shows a shadow photograph of one such sample. The glass has virtually no gas bubbles but there are striae and spherules of fused rutile. The color of the rutile precipitates ranges from dark-violet to transparent and probably de-

pends on the iron content in the natural rutile. Individual rutile spherules are present inside classical striae and are probably formed from the product of thermal decomposition of sphene. The sample contains a substantial amount of white, microscopic, often with crystalline faceting, rod-shaped formations. Microprobe analyze showed that this is zirconium oxide containing some hafnium. However, it cannot be asserted that this is zircon, since it has been shown in [6] that zircon dissociates at 1674 ± 7°C into baddeleyite and silicon dioxide.

Figure 2 shows the optical transmission spectra of glass made from quartz grains, obtained almost with the same technology used for enriching quartz raw materials but the finishing purification by means of chemical etching was conducted in one case in a solution with hydrofluoric acid and in another case by orthophosphoric acid. The transmission spectra in the UV region show that quartz raw material of this form is best enriched by means of chemical etching of impurities in a solution of hydrofluoric acid.

To establish the possibility of using the indicated quartz raw material in the production of multicomponent technical glasses, a glass with composition identical to that of electro-vacuum glass was made. The glass had the following composition: enriched quartz grains — 68%, B_2O_3 — 2.8%, Al_2O_3 — 4.0%, CaO — 7%, Na_2O — 10.0%, K_2O — 7.7%. The glass was made in air in a high-temperature furnace with chromite-lanthanum heaters in an alundum crucible at 1450°C. The glass is transparent, good quality, and slight greenish. The results of the experiment show that enriched quartz grains from the quartz wastes can be used to make technical glasses.

These investigations show that quartz sand from the dumps of the enterprise “Plast-Rifei” and be enriched quite well even using simplified technological purification schemes. Rutile and zircon are the most difficult mineral impurities to remove. These mineral inclusions can be removed by means of flotation, using different methods of gravitational separation and changing the composition and parameters of the leaching with acid.

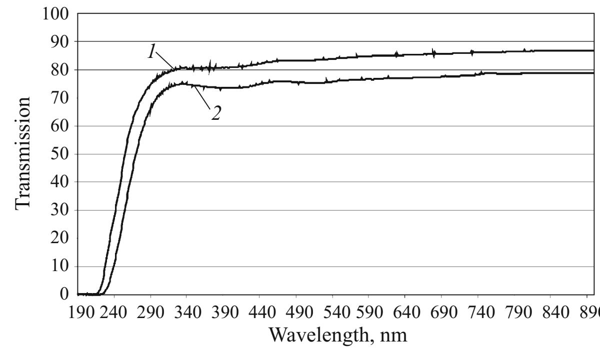

Fig. 2. Optical transmission spectra of quartz glass made from raw material enriched by means of a solution of acids: *1*) with hydrofluoric acid; *2*) with orthophosphoric acid.

In summary, it has been confirmed that quartz from the kaolin deposit Zhuravlinyi Log can be used to produce high-purity quartz concentrates, which can be used in the most high-tech products.

REFERENCES

1. A. V. Turasheva, “State and problems of mineral-raw materials resources of quartz melting raw materials in the Russian Federation,” in: *Proc. Intern. Seminar on Quartz and Silica* [in Russian], Syktyvkar (2004), pp. 178 – 181.
2. N. G. Bydtaeva, R. A. Kiseleva, and I. M. Mileeva, “Prediction-search models of deposits of especially pure quartz,” *Otechestv. Geologiya*, No. 4, 57 – 63 (2006).
3. R. Sh. Nasyrov, V. N. Bykov, A. G. Korablev, et al., “Test melts of quartz glass at a method of evaluating the quality of quartz concentrates,” *Razvedka, Okhrana Nedr*, No. 10, 46 – 47 (2007).
4. A. G. Korablev, R. Sh. Nasyrov, A. R. Shakirov, and V. N. Bykov, “Experimental study of striae in fused quartz from the Berkutinskaya vein (South Urals),” *Razvedka, Okhrana Nedr*, No. 10, 47 – 48 (2007).
5. R. Sh. Nasyrov, “Agglomeration method of purifying quartz powder,” *Obogashch. Rud*, No. 6, 14 – 16 (2009).
6. D. N. Kamaev, S. A. Archugov, and G. G. Mikhailov, “Investigation and thermodynamic description of the system $ZrO_2 – SiO_2$,” *Izv. Chelyabinsk. Nauch. Tsentra*, No. 4, 39 – 44 (2004).